

DESCRIPTION

“POLYMERIC MIXTURE COMPRISING A POLYFLUORENE DERIVATE AND USE THEREOF AS OPTICAL DEVICE.”

This invention relates to a polymer mixture of a polymer which is
5 transparent at a wavelength of at least 300 nm and a fluorene polymer
for use as an optical material. In particular, it relates to use of such
material as an optical switching device.

It is known that a polymer which is transparent to a particular
wavelength corresponds to a polymer which has good ability to transmit
10 light with weak absorption phenomena.

Polymethylmethacrylate, abbreviated as PMMA, is an acrylic
olefin polymer having high transparency and having a good ability to
transmit light. Because of its specific properties, PMMA has hitherto
been used for many years as a basic constituent for plastics fibre optics
15 and in general is commonly used as an inert base material in optical
applications.

Polyfluorene, a polymer material which is also transparent within
the visible range, is a polycyclic aromatic hydrocarbon known for its
optical emission properties in the visible when excited. In the solid state
20 such a polymer has long chains of carbon atoms with conjugated bonds
and is characterised by strong intermolecular and intramolecular
interactions which govern the absorption and emission capabilities of the
final polymer material. For example, the use of polyfluorene in the solid
state in optical devices, such as blue LEDs, is known.

25 Within the visible range, among the various fluorene polymers,

poly(9,9-dioctyl)fluorene, abbreviated to PFO, has been studied in particular, and its spectral characteristics have been described in the literature through optical photoexcitation experiments [Krabeel, B. et al., "Unified picture of the photoexcitations in phenylene-based conjugated
5 polymers: Universal spectral and dynamical features in sub-picosecond transient absorption", Phys. Rev. B 61(12) 8501 (2000)]. In particular this shows absorption wavelengths below 400 nm, stimulated emission (SE), that is a gain band, between 440 nm and 500 nm, photo-induced absorption (PA) between 510 and 650 nm, with a peak at 580 nm, and a
10 second photo-induced absorption between 660 and 850 nm with a peak at 780 nm. As a result of its spectral characteristics this has a photoluminescence graph when exposed to excitation which is characterised by a rather broad and therefore unstructured band, with specifically rather restricted stimulated emission.

15 These emission properties of fluorene polymers in the visible have on the one hand made it possible to use them in devices of the LED type, and on the other hand has prevented their use in signal production optical devices where the formation of a particular structured broad gain band in the region of interest for the device under stimulation
20 is required.

 Mixtures of polymethylmethacrylate and poly(9,9-dioctyl)fluorene have been described in the literature, specifically in the field of UV microscopy. In this case, once thin films of the mixture have been formed in initial concentrations of between 1 and 50% of PFO in PMMA
25 using the research technique known as NSOM (UV scanning near-field

optical microscopy), it has been observed that the dispersion of PFO in PMMA is inhomogeneous, separation of the two polymers predominating. No behaviour deriving from presence of the mixture has been reported. [Chappell, J. and Litzey, D.G. "Phase separation in
5 polyfluorene-polymethylmethacrylate blends studied using UV near-field microscopy", Journal of Microscopy 209, 188-193].

Surprisingly it has been found that it is possible to obtain and characterise polymer mixtures of a transparent polymer and polyfluorene having spectral characteristics which are different from those of
10 polyfluorene alone.

The object of this invention is therefore to provide a polymer mixture comprising polyfluorene which has a structured gain band making it possible to use it as an optically active material in the visible range.

15 Another object of the invention is to provide an optical material which can be used as an optical switch within the visible range.

The above objects have been accomplished through a polymer mixture of a transparent polymer and a fluorene polymer as indicated in Claim 1. Where the density of the fluorene polymer is mentioned, the
20 number of isolated chains of fluorene polymer per volume unit in cm^{-3} is meant. For values of such density, where the term "about" is used, this means a variability of ± 0.5 in the mantissa value. By optical device is meant a device capable of producing an optical signal. In this context by
"optically active material" is meant a material which is capable of having
25 a structured gain band corresponding to the stimulated emission band

for the material in the region of interest which, in the case of this invention, is the visible region.

Further features and advantages of the invention will become apparent from the following detailed description with reference to an embodiment of the invention provided purely by way of example and
5 without restriction and to the appended figures, in which:

Figure 1 is a graph of the spectral characteristics of the mixture according to the invention (-■-) and PFO in the solid state (—),

Figure 1a is a graph of the luminescence of the mixture according
10 to the invention (-■-) and PFO in the solid state (—),

Figure 2 is a graph of the photo-induced anisotropy of the mixture according to the invention, and

Figure 2a is a graph of the photo-induced anisotropy of PFO in the solid state, and

15 Figure 3 is a graph showing the normalised transmission curve for the material according to the invention in a 3-pulse experiment.

The invention therefore relates to a mixture comprising a polymer which is transparent at a wavelength of more than 300 nm and poly(9,9-XY-fluorene), wherein X and Y are each separately a straight or
20 branched C₁-C₁₂ saturated or unsaturated hydrocarbon chains and the said poly(9,9-XY-fluorene) is substantially dispersed as isolated chains having an isolated chain density in the said transparent polymer of a maximum of $1 \times 10^{19} \text{ cm}^{-3}$.

Preferably X and Y are separately a straight C₁-C₁₂ saturated
25 hydrocarbon chain, more preferably C₆-C₉, and even more preferably

they are two equally saturated straight alkyl chains.

In accordance with a preferred embodiment, X and Y are two octyl chains, in which the poly(9,9-XY-fluorene) is PFO (poly(9,9-dioctyl-fluorene)).

5 The said transparent polymer may be a polymer which is transparent in a range from 300 nm to 900 nm, and even more preferably from 320 to 750 nm. It may be selected from the group comprising polymethylmethacrylate, polystyrene, polycarbonate, and preferably it is PMMA.

10 Without wishing to be bound by any theory, the mixture according to the invention has proved to be optically active in the visible region in accordance with the objects of the invention solely through the presence of the fluorene polymer in isolated chains. It is therefore felt that the conjugation of the double bonds in the absence of inter-chain
15 interactions, typical of fluorene material in the solid state, is responsible for the stimulated emission spectrum which is different from that obtained from the conjugation which is disturbed by intermolecular interactions as will be demonstrated in detail below.

Because polymerisation of the two polymers is not desired, the
20 mixture according to the invention may be prepared by directly mixing the two component polymers in the solid state, at room temperature and pressure, in a suitable inert solvent, or the two polymers may first be changed into the liquid state and then mixed. Once a clear solution has been obtained the solvent is removed. Preferably the two polymers are
25 added in a (polyfluorene): (polymer transparent at wavelengths above

300 nm) ratio of 1:10.

In a further aspect the invention also relates to a solid optically active polymer material of the mixture according to the invention.

Preferably the said optically active solid material is a film of the mixture according to the invention. Even more preferably it is a thin film having a thickness of less than 1 μm which has a gain band between 450 and 610 nm with a maximum gain of 2500 db/cm. In a further aspect the invention also relates to use of such optically active polymer material as a switching device according to Claim 17. Preferably for this purpose the optically active polymer material is in the form of a polymer film of the mixture and has a gain modulation of about 100 nm between 530 and 610 nm.

The invention will now be described in detail with reference to an example of the preparation of a solid polymer film and a number of tests to evaluate the optical characteristics of the material, as well as an experimental test for evaluating the optical material as an optical switch. The preparation example and the experimental tests are provided by way of an example of the invention and must not in any way be interpreted as restricting the invention, those skilled in the art being in a position to propose changes and modifications, all of which will fall within the scope of the appended claims.

Example 1

50 mg of polymethylmethacrylate and 5 mg of poly(9,9-dioctylfluorene) and 1,2 ml of toluene were placed in a glass vial in sequence. The compounds were added at room temperature and

pressure. The solution was then heated to a temperature below the boiling point of toluene in order to dissolve the solids completely. Once the solution was clear it was deposited onto a glass substrate using the drop cast technique, which comprises deposition of the mixture in the liquid phase onto the substrate by dropwise addition of the solution and evaporation of the solvent, in this case toluene, in a closed environment, for example a glass bell, to avoid external contamination.

A polymer film having a thickness of about 1 μm was thus obtained.

This film was then subjected to a number of experiments in order to demonstrate its optical properties.

Example 2: Investigation of the spectral characteristics of the optical material

The solid film obtained in Example 1 was subjected to a conventional pump-probe experiment [Lanzani, G. et al., "Photophysics of methyl-substituted poly(para-phenylene)-type ladder polymers) in Semiconducting Polymers – Chemistry, Physics and Engineering, P. Van Hutten, Wiley-VCH, Weinheim, 235 (2000)]. In this technique the sample was excited by two different pulses – a less intense probe pulse and the other a very intense pump pulse to evaluate the normalised transmission of the probe in the presence or absence of the pump pulse. The film was therefore subjected to two pulses in the absorption band for solid PFO, the first pump pulse corresponding to 390 nm and the second probe pulse corresponding to continuous white light (440-1000 nm), with a probe delay of 2 ps. The (-■-) curve in the graph in Figure 1

was obtained, where wavelength is shown as the abscissa and the transmission value of the standard probe ($\Delta T/T_{\text{without pump}}$) is shown as the ordinate, where ΔT is $T_{\text{pump}} - T_{\text{without pump}}$. With reference to Figure 1, the material according to the invention had a very wide structured SE band from 430 to 610 nm with peaks at 470 nm, 500 nm and 540 nm, with the onset of photo-induced absorption at 680 nm. This was then compared with the (---) curve generated by PFO in the solid state, and the gain band of the polymer film in the visible region from 450 nm to 610 nm was obvious. As indicated above, broadening of the gain band in the stimulated emission region corresponding to visible wavelengths demonstrated the advantageous optical properties of the material according to the invention, which is therefore described as an "optically active" material.

The gain (g) for a film of thickness d was obtained directly by pump-probe measurements. The following relationship was used in order to obtain the measurement in decibels (db):

$$g(\text{db}) = 10 \log_{10} \left(\frac{\Delta T}{T} + 1 \right)$$

The $\Delta T/T$ values were obtained from the graph in Figure 1 and the various gain values were extrapolated. Three examples of gain values corresponding to three different values of $\Delta T/T$ are shown in the table below:

Wavelength	Gain
450 nm	2500 db/cm
530 nm	860 db/cm
610 nm	0 db/cm

The density of the isolated chains was then estimated, and this was defined as N_0 . This was estimated by pump-probe measurements made on the sample using the following procedure. The following
 5 formula was used to calculate N_1 , corresponding to the number of excited states.

$$\Delta T/T = \sigma_{1-n} N_1 d$$

where $\sigma_{1-n} = 1.4 \times 10^{-16} \text{ cm}^2$ is the impact cross-section of the $S_1 - S_n$ transition (from the first to the nth state of the excited singlet), and

10 $d = 1 \text{ }\mu\text{m}$, and is the film thickness.

The value of $\Delta T/T$ at 680 nm, corresponding to the $S_1 - S_n$ transition, was obtained from the $\Delta T/T$ spectrum shown in Figure 1, and this was equal to about 0.012. Thus using the formula above the value of N_1 was obtained, and this was equal to about $8 \times 10^{17} \text{ cm}^{-3}$. The
 15 density of the isolated chains in the fundamental state, N_0 , was calculated from the following formula

$$N_0 = N_1 / (F \times \sigma_{0-1})$$

where $\sigma_{0-1} = 6 \times 10^{-16} \text{ cm}^2$ is the transverse cross-section of the $S_0 - S_1$ transition (from the fundamental state to the first excited state of the
 20 singlet), and

$F(3 \times 10^{14} \text{ cm}^{-2})$ is the photon flow per excitation pulse and N_1 and N_0 have the meanings given above.

Therefore making the substitutions, in the example at 680 nm, a density of about $5 \times 10^{18} \text{ cm}^{-3}$ was obtained.

25 The experiment was repeated with other values of $\Delta T/T$ and

density values within the range from about 1×10^{18} and about $6 \times 10^{18} \text{ cm}^{-3}$ were obtained.

The photoluminescence spectrum of the optical material according to the invention (-■-) was also measured and shown in Figure 1a and this was compared with the spectrum for PFO (----). As will be seen from Figure 1a, the material according to the invention had a more structured spectrum than the spectrum of PFO alone, which was less well-defined.

In confirmation of the fact that the optical properties of the optical material according to the invention are clearly different from those of PFO, in the course of performing the pump-probe experiment, photo-induced anisotropy was also measured using conventional techniques. The results are shown in Figure 2 (for the material according to the invention) and in Figure 2a (for PFO), where anisotropy is shown as the ordinate and time as the abscissa. The evaluation was performed at wavelengths of 680 nm (___), 470 nm (-■-) and 560 nm (-□-). As will be seen from the appended figures, the anisotropy of the material according to the invention at different points in the visible spectrum was constant over time in comparison with PFO in the solid state, which quickly lost its polarisation when subjected to excitation.

The surprising optical results for the material according to the invention, which having a gain band in the visible finds application as an optically active material at those wavelengths, are clear from the examples above.

Example 3: 3-pulse experiment

The film obtained according to Example 1 was subjected to a 3-pulse experiment. This test comprises repeating the two probe-pump pulse experiments described above and adding a further signal described as a push signal. The polymer film was therefore subjected to the following three signals – a pump signal at 390 nm, a probe signal at 590 nm and a push signal at 780 nm. The push signal was introduced about 1.5 ps after the pump signal. Normalised transmission ($\Delta T/T_{\text{without pump}}$) of the probe signal (-□-) is shown in the graph in relation to the probe delay, as shown in Figure 3. The curves for normalised transmission in the two pulse experiment (___) and the push signal (---) are also indicated. With reference to the transition curve for the probe signal in the two pulse experiment (___) it will be seen that this overlaps the push signal curve (----). Analysing the progress of the transmission curve for the probe (-□-), the sum of the effects of these two signals brought about instantaneous cancellation of the positive gain signal after about 2 ps, which subsequently increased again, although with a normalised transmission which was less than the probe transmission in a two pulse experiment (___). The surprising result of having a gain which was cancelled out when a further pulse was applied has suggested use of the polymer material according to the invention as an optical switch. Switching occurred in a narrower band of about 100 nm, from 530 nm to 610 nm. Because the recovery kinetics found were completed in about 2 ps, optical modulation operated at a frequency of 300 GHz. Without wishing to be bound by any theory, the behaviour of the optical switch was explained by assuming that the third push pulse

separated the excited states of the fluorene into a single chain forming charges. The absorption signal from the latter therefore completely cancelled out the gain signal (stimulated emission band) and with recombination of the charges the gain signal of course reappeared.

- 5 From the experiments described in Example 2 and Example 3 in combination with Figures 1 and 3 it is clear that the surprising formation of a well-structured gain band in the visible means that the mixture according to the invention can be used as an effective fast optical device. In particular this invention makes it possible to design optical
- 10 switches, and also electro-optical switches through applying an electrical field capable of generating charges which cancel out the gain signal only instantaneously to the optical device of the polymer mixture with isolated polyfluorene chains.